

LOW THERMAL EXPANSION COATINGS FOR CARBON/CARBON COMPOSITES

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Abstract

Two classes of materials are considered for low expansion protective coatings for carbon/carbon composites. They include composites containing particles which undergo allotropic phase transformations accompanied by negative volume changes with increasing temperature and anisotropic oxides which demonstrate low expansion due to microcracking. Conditions for failure of coatings by either cracking or spallation due to thermal mismatch are evaluated.

1. Introduction

Many properties of carbon-carbon composites are attractive for highly stressed, structural applications at high temperatures. They have low density and good strength and toughness at temperatures up to 2735°C (5000°F). For use in oxidizing environments, however, they must be protected from oxidation by a coating or additive which forms a protective scale or inhibits the oxidation process in some manner. The task of coating these composites is complicated by their very low and anisotropic thermal expansion. In fact, much of the work on coatings for these materials has centered around accommodating, or alleviating the consequences of, differential thermal expansion between the coating and the carbon/carbon substrate.

Several approaches have been based upon the use of SiC as the primary coating component.[1,2] There are numerous advantages: (1) SiC is compatible with C; (2) the surface of the composites can be readily converted to the carbide; (3) the thermal expansion of SiC is relatively low; and (4) upon oxidation, SiC forms a dense, protective scale of SiO₂. However, these coatings invariably crack on cooling. The most successful approaches have utilized glass sealants which wick into and seal cracks, but such systems are vulnerable at temperatures below the softening point of the glass and at very high temperatures due to low viscosity and volatilization. Alternate approaches have been suggested which consist of multiple layers in which the thermal expansion is graded from the substrate

to the coating surface. Such coatings can decrease interfacial shear stresses; however, they will do nothing to alleviate the tensile stresses in the coating. Improving the thermal expansion match would decrease the temperature at which cracking occurs and decrease the size (and number) of cracks at any particular temperature. In the ideal case, no cracking would occur. Unfortunately, the average in-plane coefficient of thermal expansion (CTE) of the composites is so low ($\alpha = 1 \times 10^{-6}/^{\circ}\text{C}$) that there are few materials with comparable expansion.[3]

The choices for applications at temperatures $> 1650^{\circ}\text{C}$ (3000°F) are even more limited. Most of the more refractory coating materials have substantially greater expansion coefficients than SiC. At the same time, the viscosity of most glass systems is too low to be of use, accentuating the need for a better expansion match. Although low expansion coatings are desirable, it should be noted that the cross-ply expansion of the composites is larger than the longitudinal by an order of magnitude, hence a CTE which is a good match for the ply surfaces is a very poor match for the edges, with residual stresses that will tend to cause spalling of the coating or delamination of the composite.

An obvious requirement of a coating system is chemical compatibility with the matrix. The two materials in contact should be stable (i.e. there should exist a two-phase field for the substrate and coating materials with low mutual solubilities) or should form a compound, or series of compounds, which has low diffusivities for components of both the coating and substrate. Alternatively, an interlayer can be deposited, which then must satisfy the same requirements with respect to both the coating and the substrate. If the diffusivities and solubilities of the various components in the interlayer are low enough that the layer can be quite thin, mechanical compatibility is unnecessary. This is only feasible if the reaction rate of the coating with the substrate is sufficiently low that widely scattered breaks in the interlayer are tolerable.

A hypothetical coating system might then consist of an outer coating which is protective (stable in an oxidizing environment, low diffusivities for oxygen, carbon and species comprising the interlayer) and mechanically compatible with the substrate, and an interlayer which is chemically compatible with both the substrate and the coating and sufficiently thin that it need not be mechanically compatible. Such an approach allows consideration of coatings which are not chemically compatible with the substrate. Chemical compatibility and interlayer considerations will not be dealt with here. The objective of this work is to examine the feasibility of two alternative approaches to obtaining low expansion coatings for carbon/carbon composites.

The first approach uses substances which undergo solid-state phase transformations which are accompanied by a decrease in molar volume in going from the low temperature to the high temperature phase. Such substances provide a lower effective thermal expansion over any temperature range containing the transformation temperature. The most useful would be those that undergo displacive (martensitic) transformations, since they are directly reversible, diffusionless and stress-dependent.

The second approach considered here centers around two families of highly anisotropic compounds which demonstrate anomalously low thermal expansion for many of the same reasons as do carbon/carbon composites: a high degree of thermal expansion anisotropy.

The mechanisms by which the low expansion derives will be discussed first. Subsequently, estimates of thermal expansion strains will be provided for each of the proposed systems. In addition, considerations for processing and temperature limitations will be discussed.

2. Mechanisms for Low Expansion Solids

2.1 Allotropic Transformations

Allotropic phase transformations, in which crystals undergo a change in structure with temperature, are, in general, accompanied by volume changes. If the volume changes are negative with temperature increase, one can hypothetically develop a coating or bulk solid in which a crystallographic transformation provides a net near-zero expansion. Understandably, the volume contraction must occur over a range of temperatures in order to reduce thermal strain transients over a large temperature range. The transformation must also be reversible, to minimize thermal mismatch on cooling from elevated temperatures, and, consequently, to prevent spalling of the coating.

High temperature ceramics which undergo allotropic transformations are listed in Table 1 along with the temperatures over which the transformations take place and the sign of the volume change during transformation.[4-6] From the tabulation, candidate materials for coatings can be selected. They include BaTiO_3 , Eu_2O_3 , GdNbO_4 , HfO_2 , Sm_2O_3 and ZrO_2 .

In assessing these candidate materials, the following conclusions are drawn: The transformation in BaTiO_3 occurs at too low a temperature (160°C) to be useful over a wide temperature range. The remaining five materials can be considered for a coating application, although Eu_2O_3 , GdNbO_4 and Sm_2O_3 are not readily available. Those which appear to be best suited for coating carbon/carbon substrates are ZrO_2 and HfO_2 , both of which undergo two allotropic transformations: from monoclinic symmetry at room temperature to the tetragonal form at intermediate temperatures and finally to cubic symmetry prior to melting. As can be seen from thermal expansion curves in Figure 1, both materials demonstrate a volume contraction during heating. For our purposes, the HfO_2 will be less effective than ZrO_2 since the volume contraction of HfO_2 during the transformation is significantly less than ZrO_2 and produces a net expansion over a temperature range of interest. However, the use of HfO_2 cannot be precluded, since the transformation temperature occurs at temperatures more than 600° higher than ZrO_2 , and thus, may be useful for higher temperature applications (i.e., $T > 2000^\circ\text{C}$).

Because of the interest in zirconia for structural and electronic applications, there is wealth of characterization data on the ZrO_2 phase transformation. It is expected that these ideas may be extended to HfO_2 systems for the present purpose. The tetragonal-to-monoclinic transformation temperature, M_s , in ZrO_2 generally decreases with particle

size or grain size, as has been well documented.[7,8] For unconstrained powders, the transformation may be spread over 600° with crystallites on the order of 20 to 30 nm (Figure 2). Muller and Muller have proposed a method to predict the size - transition temperature behavior for ZrO_2 powders based upon an energy argument, where the size effect for unconstrained ZrO_2 particles (powders) derives from surface tension.[9] For ZrO_2 contained in a rigid matrix, the constraint is provided from the elastic tension in the matrix. The latter has been discussed in detail by Heuer et al. and demonstrated for $\text{Al}_2\text{O}_3\text{-ZrO}_2$ in Figure 3.[10] In general, the phase transformation occurs at a lower temperature on cooling than on heating. For unconstrained powders, the particle size effect on the transformation temperature during cooling is slight, but much more pronounced during heating [9] (Figure 4). Similar data for constrained systems are not available.

The transformation temperatures for both ZrO_2 and HfO_2 are also highly dependent upon the concentration and amount of stabilizing agent present. In these materials, MgO , CaO and Y_2O_3 , or other rare earths, are added to stabilize the high temperature structure. Specifically, Claussen reports that "additions of stabilizers, especially the high solvent types (Y_2O_3 and most rare earth oxides), will shift M_s to lower temperatures for a given particle size." [11] For ZrO_2 , the monoclinic-to-tetragonal transformation may vary from 950 to 1220°C. For HfO_2 the same transformation varies from 1610 to 1799°C.[5] By using ZrO_2 and HfO_2 with varying amounts and types of stabilizing agents, it should be possible to grade the transformation over a series of temperatures. Although much of the information contained in the literature is clouded by a combination of size and stabilizer effects, it is clear that the transformation temperature is a variable which can be controlled and graded by size and impurity content.

2.2 Anisotropic Oxides

A second method of producing low expansion solids uses the anisotropic nature of selected oxides. The pseudobrookite structures are among the most highly anisotropic of oxides, with extremely small (or negative) thermal expansion coefficients in the "a" direction and very large coefficients of thermal expansion in the "c" direction, as reviewed by Bayer.[12] Due to the large degree of anisotropy, these materials often spontaneously microcrack on cooling from processing temperatures when grain sizes are large and greater than some critical size. The thermal expansion of the microcracked materials is near zero because the microcrack openings accommodate the expansion.[13] It is only when the crack openings are filled by the expanding grains that a net positive expansion results. Since the phenomenon is expected to hold for any material with a large degree of thermal expansion anisotropy, numerous possibilities exist for low expansion coatings. A loss of mechanical integrity may result due to microcracking, since grain growth is difficult to avoid and microcracks form on the order the grain size, 50 to 70 μm for some pseudobrookites.[14] Such microcracks coalesce and act as sources of failure.

One method of retaining low expansion features of the microcracked pseudobrookites while improving the mechanical properties is by combining these materials with constituents which undergo allotropic transformations. Claussen produced AlTi_2O_5 with the addition of unstabilized ZrO_2 to serve

as a model of a low-expansion, microcracked material having no loss in mechanical strength.[11] The ZrO_2 particles, on undergoing the transformation from tetragonal-to-monoclinic symmetry on cooling, cause microcracks to form along AlTi_2O_5 - ZrO_2 boundaries. The microcracks are now on the order of the ZrO_2 grain size ($< 5 \mu\text{m}$) and provide no significant reduction in fracture strength.

Table 2 lists oxides having the pseudobrookite structure and their melting points. From this list it is clear that a few of these pseudobrookites may be considered for a coating materials, namely Fe_2TiO_5 and MgTi_2O_5 which melt above 1500°C . A possible series of higher temperature pseudobrookites may be synthesized by substitution on the cation sites, such as $\text{MgTi}_{1.6}\text{Zr}_{0.4}\text{O}_5$, but its properties have not been measured. In addition to the pseudobrookites, other oxides which are expected to exhibit this behavior include Nb_2O_5 and any other non-cubic oxides with high anisotropy. The thermal expansion behavior for Nb_2O_5 is shown in Figure 5. Note that two expansions for Nb_2O_5 are shown, indicative of grain size (microcracking) effects. The lower expansion material exhibits a mean expansion coefficient of $0.92 \times 10^{-6}/^\circ\text{C}$.

Other notable low expansion solids are compositions in the series $\text{Na}_{1-x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ and $\text{Na}_{1-4z}\text{Zr}_{2-z}\text{P}_3\text{O}_{12}$ where $0 < x < 1$ and $0 < z < 0.5$, as designed and studied by Alamo and Roy.[15] These materials have a characteristic rigid framework with an open structure which allows for large cation substitution. Like the pseudobrookites, these materials are characterized by a negative thermal expansion coefficient in the "a" direction and a strongly positive expansion in the "c" direction. To date, the coefficients of thermal expansion have not been measured above 600°C (Figure 6) nor has the presence of microcracking been established. Although numerous possibilities exist for cation substitution in these materials, the present materials have melting points in the 1300 to 1500°C range. Higher melting compounds would be required for the present application.

3. Discussion

Consideration of the behavior of coatings on carbon/carbon composites is complicated by the nature of the composites. The thermal expansion of the yarn bundles is negative along the longitudinal axis and positive in the transverse direction while that of the matrix is less than the transverse expansion of the fibers but positive and isotropic. Consequently, the composites are highly microcracked. The thermal expansion (and mechanical response) may be very different on the local micro-scale than it is on the macro-scale based upon measured thermal expansion coefficients. Nonetheless, the general behavior of current systems is qualitatively consistent with a simple description which considers the composite to be homogeneous and planar isotropic and mismatch strains to be confined to the coating (composite thickness \gg coating thickness). While recognizing the limitations, such an analysis will be used here to provide a simple, if approximate, evaluation of alternative coatings.

The differential strain is assumed to be entirely confined to the coating and may be written as

$$\Delta\epsilon = (\alpha_c - \alpha_s)(T_e - T) \quad (1)$$

where α_c is the coefficient of thermal expansion of the coating, α_s is the CTE of the substrate, T_e is the equilibrium temperature at which the coating and substrate have no thermally induced differential strains, and T is the temperature of interest. The equilibrium temperature will be approximately the temperature at which the coating was applied or the maximum temperature at which the system has been annealed.

Thermal expansion of a typical two dimensional carbon/carbon composite is shown in Figure 7(a). The expansion is negative at temperatures below 250°C and reaches a maximum of $\alpha_{s,max} = 2.7 \times 10^{-6}/^\circ\text{C}$. [4] Averaged over the entire range, the mean expansion coefficient between room temperature and 1370°C is $\alpha_s = 1 \times 10^{-6}/^\circ\text{C}$. However, a more accurate approximation, as illustrated in Figure 7(b), is

$$\text{when } \alpha = 0 \quad 0 < T < 700^\circ\text{C}$$

$$\text{when } \alpha = 2.16 \times 10^{-6}/^\circ\text{C} \quad 700^\circ\text{C} < T < 2000^\circ\text{C}$$

The cross-ply (transverse) expansion is much higher at $\alpha_T = 10^{-5}/^\circ\text{C}$.

To illustrate the magnitude of the thermal strains in conventional coatings, consider the thermal mismatch between carbon/carbon and SiC. A typical two-dimensional carbon/carbon composite demonstrates about 0.3% tensile strain-to-failure. For the purpose of this discussion, the usable strain will be taken to be 0.2%. Bulk SiC fails at approximately 0.1% tensile strain and about five times that in compression. In a thin coating, however, it is unlikely that the compressive strain would exceed 0.3% due to buckling. Assuming that the thin coating approximation applies, Figure 8(a) may be used to determine the total strain (both mechanical and thermal) in the coating by measuring the difference between the SiC and carbon/carbon expansion contours for the appropriate loading condition and temperature. The only temperature at which there is no thermal strain in the coating is that at which the lines representing SiC and carbon/carbon cross at zero mechanical strain (Point A). This would be the coating application temperature, here chosen to be 850°C. In the unloaded state, as the temperature is lowered, the strain in the coating is increasingly tensile until approximately 500°C where the tensile strain to failure of the coating is exceeded, and the coating cracks (Point B). The cracks increase in width and frequency as the temperature is further decreased. As the temperature is again increased, the coating, now cracked, can sustain no tensile load, and the cracks do not close until the coating is placed in compression ($T > 850^\circ\text{C}$). However, if the composite is stressed to its maximum usable strain, however, the cracks do not close until approximately 1800°C (Point C). Spallation becomes a problem above 1800°C under no applied load when the maximum allowable compressive strain is reached (Point D). The problem is much more severe for oxides (Figure 8(b)), and is significantly better only for low expansion ceramics such as Si_3N_4 and BN listed in Table 3.

A coating which matched the composite in the higher temperature region would be subjected to differential thermal strains of 2.16×10^{-6} only at $T < 700^\circ\text{C}$. This is below the temperature at which the composite oxidizes appreciably. Cross-ply strains would be about 15% lower due to the higher CTE of the coating, but still too high.

The problem at the edges, however, would be quite severe. In the same example cited above, the differential expansion, calculated from the transverse expansion of carbon/carbon, would result in a residual compressive strain in the coating $> 0.4\%$ at room temperature. Clearly, spalling or delamination will result. The latter is a possibility because the thin coating approximation may be inappropriate at the edges in some systems due to the following reasons: 1) conversion coatings often penetrate along the plies to depths comparable to, and even greater than, the thickness of the composite; and 2) while the cross-ply compliance is high, the cross-ply tensile strength is typically very low, 1 ksi. This situation seems to require that the edges be dealt with in a different manner, perhaps by coating with a different but compatible material.

3.1 CTE Reduction by Allotropic Transformations

Unstabilized ZrO_2 , and presumably any other compound undergoing large anisotropic volume changes upon transformation, spontaneously fractures during the transformation. Therefore, a coating would have to consist of a composite of transformable particulates in a constraining compatible matrix, exactly analogous with transformation toughened ceramics. In fact, such ceramics are commercially available and are superior in applications requiring good thermal shock resistance - a consequence of both improved toughness and reduced thermal expansion.[16]

To estimate the CTE of a composite material, one would first establish the requirement for mechanical equilibrium that the sum of the forces over an area will be zero:

$$A_1 E_1 \epsilon_1 + A_2 E_2 \epsilon_2 = 0 \quad (2)$$

where,

$$\epsilon_i = (\bar{\alpha} - \alpha_i) \Delta T \quad (3)$$

and A_i is respective area fraction. By substituting Eqn.(3) into Eqn. (2), and replacing the area fraction by the volume fraction, V_i , results in an approximation for the mean CTE for a composite:

$$\bar{\alpha} = \frac{\alpha_1 V_1 E_1 + \alpha_2 V_2 E_2}{V_1 E_1 + V_2 E_2} \quad (4)$$

The apparent average thermal expansion coefficient of the ZrO_2 between RT and 1500°C is $-1.35 \times 10^{-6}/^\circ\text{C}$. As an example, without regard to chemical compatibility, if the matrix were SiC, where $\alpha_{\text{SiC}} = 4.5 \times 10^{-6}/^\circ\text{C}$, a coating containing 40 v/o ZrO_2 would have $\bar{\alpha} = 2.76 \times 10^{-6}/^\circ\text{C}$. A coating consisting of approximately 50 vol.% ZrO_2 particulates in SiC would match

the high temperature region of the carbon/carbon expansion curve perfectly, virtually assuring that cracking would occur at innocuous temperatures. It should be noted that if the moduli were equal, 40 vol.% ZrO_2 would be sufficient to match the expansions.

Another consideration for the successful implementation of allotropic transformations for low expansion coatings relies on the production and maintenance of fine ZrO_2 crystallites in the matrix, based upon the size temperature relation for the specific matrix. Clearly, during use, these particles cannot coarsen least they grow to the extent where M_s is independent of temperature, as in Figure 4. The materials would then be unsuitable for temperature cycling. A grain size - time relation should be well-established as a function of temperature for the particular ZrO_2 system.

This approach to thermal expansion control also provides a straightforward means of dealing with the edge problem. The edges could be converted or coated with a different but compatible material, while the plane surfaces would be coated with the low expansion composite described above. If the low expansion material were SiC-ZrO_2 , possible choices for the edges might be pure SiC , or perhaps for an even better match, SiC with a high volume fraction of stabilized ZrO_2 , or even ZrC followed by ZrO_2 . Following the above analysis, a composite of $\text{SiC-40 vol.}\%$ stabilized ZrO_2 would demonstrate $\bar{\alpha} = 7.6 \times 10^{-6}/^\circ\text{C}$, where α for stabilized $\text{ZrO}_2 = 15 \times 10^{-6}/^\circ\text{C}$. Such a value would provide a reasonable match with the cross-ply expansion of the composite. To obtain such a structure one might deposit stabilized ZrO_2 to the edges of the composite alone at some point in the coating process.

The use of higher expansion compounds for coatings might also be made more viable by using this approach. For example, while Al_2O_3 has $\alpha = 9 \times 10^{-6}/^\circ\text{C}$, a composite $\text{Al}_2\text{O}_3\text{-50 vol.}\%$ ZrO_2 would have $\alpha = 4.7 \times 10^{-6}/^\circ\text{C}$. The mismatch is by no means eliminated but is comparable to that for SiC . Finally, the use of HfO_2 would extend the useful range of the phenomenon to temperatures exceeding 1650°C (3000°F).

3.2 CTE Reduction with Anisotropic Oxides

The thermal expansion behavior of these compounds, as shown in Figure 5, can be qualitatively identical to that of carbon/carbon composites. It should be possible to obtain a near perfect match in the plane of the fabric. Following the above discussion, the primary mechanical problem will be with the edges. Coating the edges with a compatible isotropic oxide would provide the proper expansion match. There remains a problem with the interface between the coatings. However, interdiffusion between the two oxides might provide a sufficiently gradual change in properties so as to avoid cracking.

Chemical interactions in these systems may be precluded by use of a fine layer of SiC , as discussed in the preceding section. Of equal importance is microstructural control because of the potential crack interaction during microcracking which may ultimately expose the carbon/carbon substrate to the atmosphere. The interaction of microcracks can be controlled by (a) the volume fraction of microcracks present, (b) the size

of the microcracks with respect to grain size, and (c) the orientation of microcracks. If ZrO_2 is used to nucleate microcracks, both the size and volume fraction of microcracks are easily controlled by the amount and size of the ZrO_2 added to the system. The orientation of microcracks is not as easily regulated, but is statistical in nature, based on the strength and orientation of boundaries with respect to the thermal and mechanical stresses. The orientation of weak boundaries may be controlled through processing, as is often seen in CVD processes.[16]

4. Conclusions

Two potential materials which demonstrate low expansion for carbon/carbon protective coatings include (a) composites containing particles which undergo allotropic phase transformations which are accompanied by negative volume changes with temperature and (b) anisotropic oxides which produce low expansion through microcracking.

To achieve low thermal expansion coatings by use of allotropic transformations, a distribution in ZrO_2 particle size is required to produce the transformation over a wide temperature range. The ZrO_2 must also be constrained by a relatively low expansion matrix. Chemical reactions between the coating and substrate, and within the multiphase coatings, must be avoided.

Coatings produced from anisotropic oxides require microstructural control to preclude microcrack coalescence and exposure of the carbon/carbon substrate. The size of microcracks may be controlled by incorporation of fine-grained unstabilized ZrO_2 which acts as a microcrack nucleation site, the size of which establishes the microcrack size.

Cursory experiments are warranted to establish the coefficients of thermal expansion, the chemical reactivity and the temperature restrictions of the proposed systems.

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Table 1: Ceramic Materials Undergoing Allotropic Transformations

Material	Temperature(°C)	Transformation	Volume Change	Ref.
BaTiO ₃	120	tetragonal - cubic	negative	4
BeO	2049	hexagonal - tetragonal	positive	4,5
Bi ₂ O ₃	730	monoclinic - tetragonal	positive	4
Dy ₂ O ₃	2200	cubic - hexagonal	positive	4,5
Eu ₂ O ₃	1075	cubic - monoclinic	negative (?)	4,6
	2120	monoclinic - hexagonal	positive	
GeO ₂	1005	tetragonal - hexagonal	positive	5
GdNbO ₄		monoclinic - tetragonal	negative	4
HfO ₂	1620	monoclinic - tetragonal	negative	5
	2700	tetragonal - cubic	negative	
Nb ₂ O ₅	1100	orthorhomb - monoclinic	positive	5
Nd ₂ O ₃	840	cubic - hexagonal	positive	4,5
Pr ₂ O ₃	880	cubic - hexagonal	negative (small)	4,5
SiO ₂ (quartz) (tridymite) (cristob.)	572	trigonal - hexagonal	negative	5
	867	hexagonal - orthorhomb.	positive	
	272	tetragonal - cubic	positive	
Sm ₂ O ₃	980	cubic - monoclinic		4,5
	2300	monoclinic - hexagonal	net positive	
Tb ₂ O ₃	1850	cubic - monoclinic		4,5
	2160	monoclinic - hexagonal		
TiO ₂	642	anatase I - anatase II (both tetragonal)	none	5
	915	anatase II - rutile (both tetragonal)	negative	
	1150	anatase III - rutile (both tetragonal)	negative	
	1299	rutile - brookite (tetragonal - orthorhombic)	positive	
ZrO ₂	1240	monoclinic - tetragonal	negative	5
	2370	tetragonal - cubic	negative	

Table 2: Melting Points of Pseudobrookites

Material	Melting Point
Al_2TiO_5	Dissociates to Al_2O_3 and TiO_2 at 1300°C
Ga_2TiO_5	1160°C (d)
Fe_2TiO_5	$> 1550^\circ\text{C}$
HfTiO_4	2100°C
MgTi_2O_5	1690°C
$\text{MgTi}_{1.6}\text{Zr}_{0.4}\text{O}_5$?
MgFeNbO_5	Decomposes under 1020°C
MgFeTaO_5	?

Table 3: Thermal Expansion Behavior for Selected Low Expansion Ceramic Materials

Material	Coefficient of Thermal Expansion ($\text{m/m}/^\circ\text{C}$)	Melting Point
SiC	4.5×10^{-6}	2700°C
Si_2ON_2	3.7×10^{-6}	?
Si_3N_4	3.0×10^{-6}	1900°C
BN	1.8×10^{-6}	3000°C (sl)
SiO_2	0.5×10^{-6}	1713°C

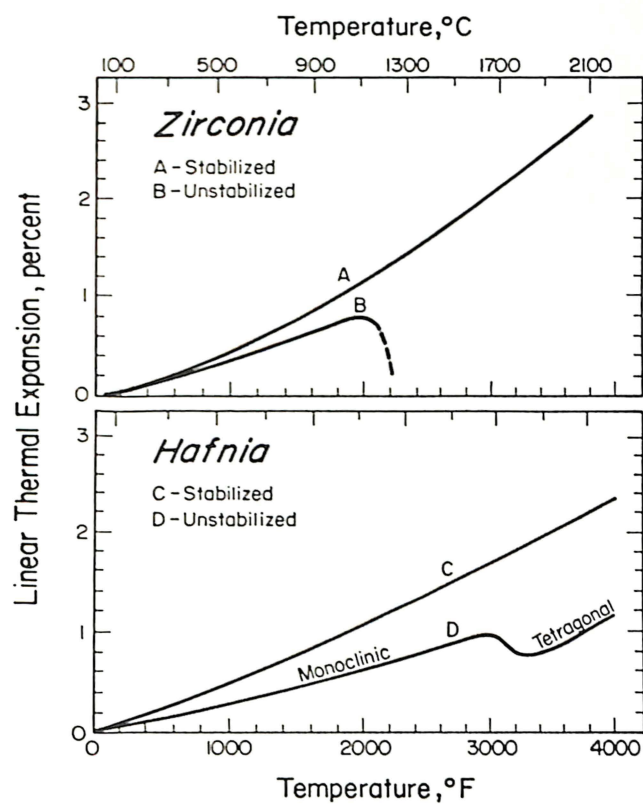


Figure 1. Linear thermal expansion of ZrO_2 and HfO_2 (from ref. 5).

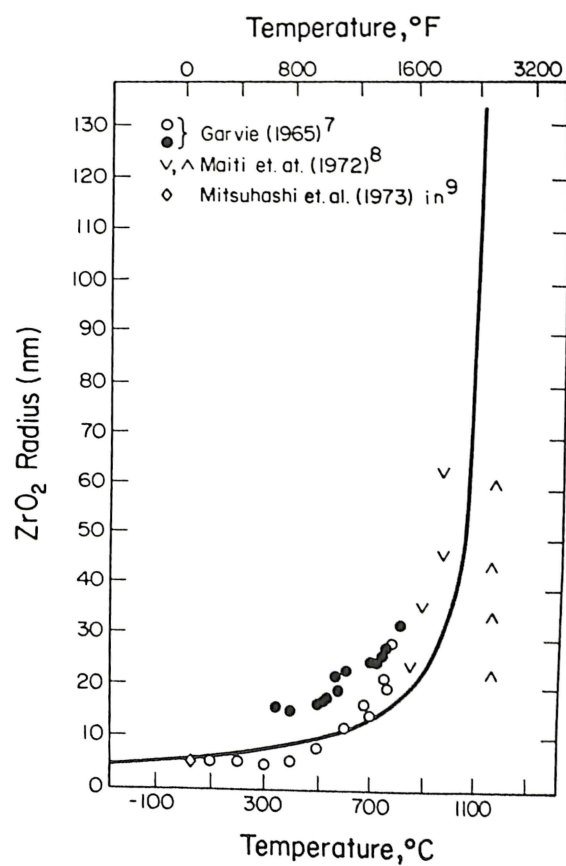


Figure 2. Transformation temperature as a function of ZrO_2 particle size in the unconstrained state (from ref. 9).

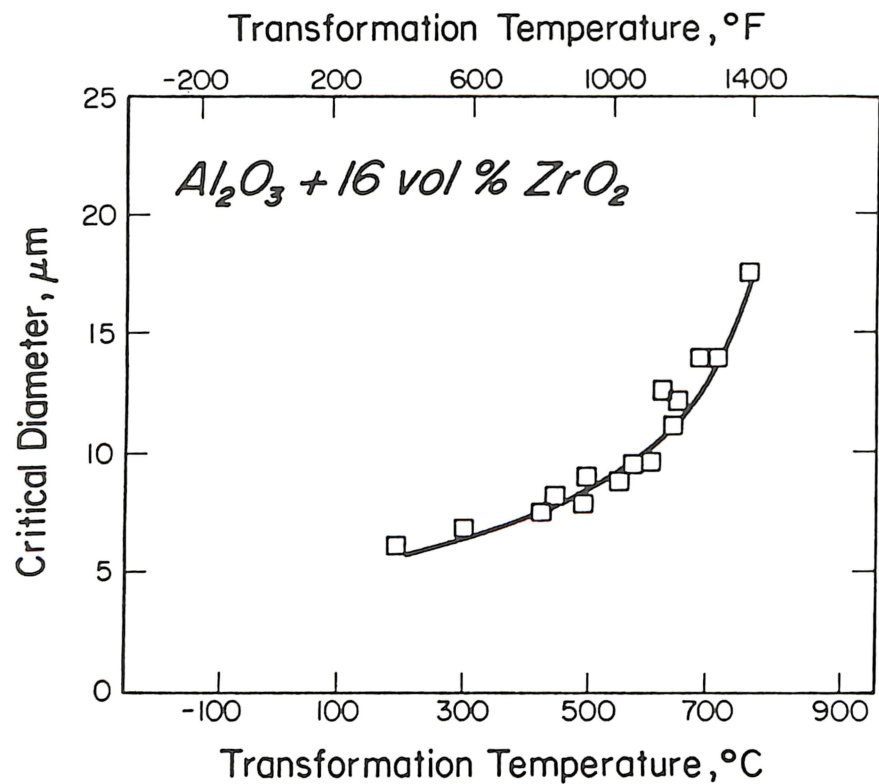


Figure 3. Transformation temperature as a function of ZrO_2 particle size in an Al_2O_3 matrix (from ref. 10).

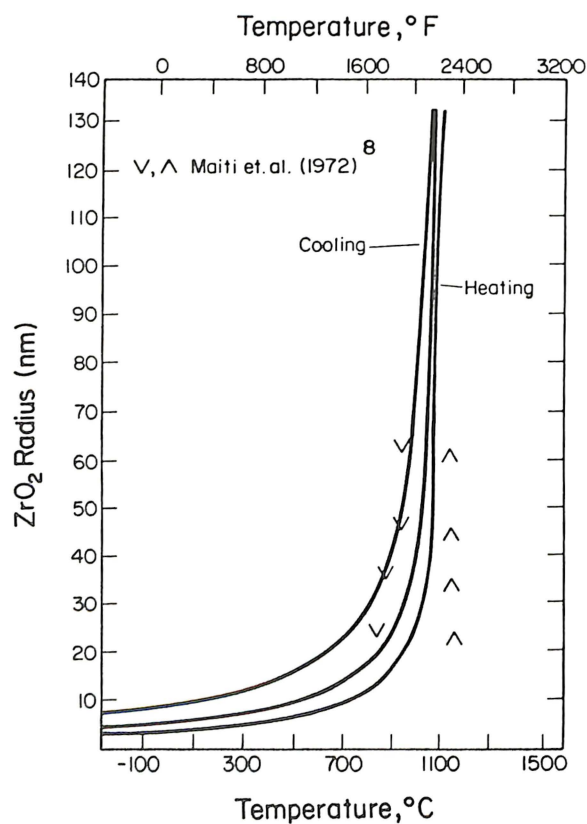


Figure 4. Variation in transformation temperature on heating and cooling for unconstrained ZrO_2 (from ref. 9).

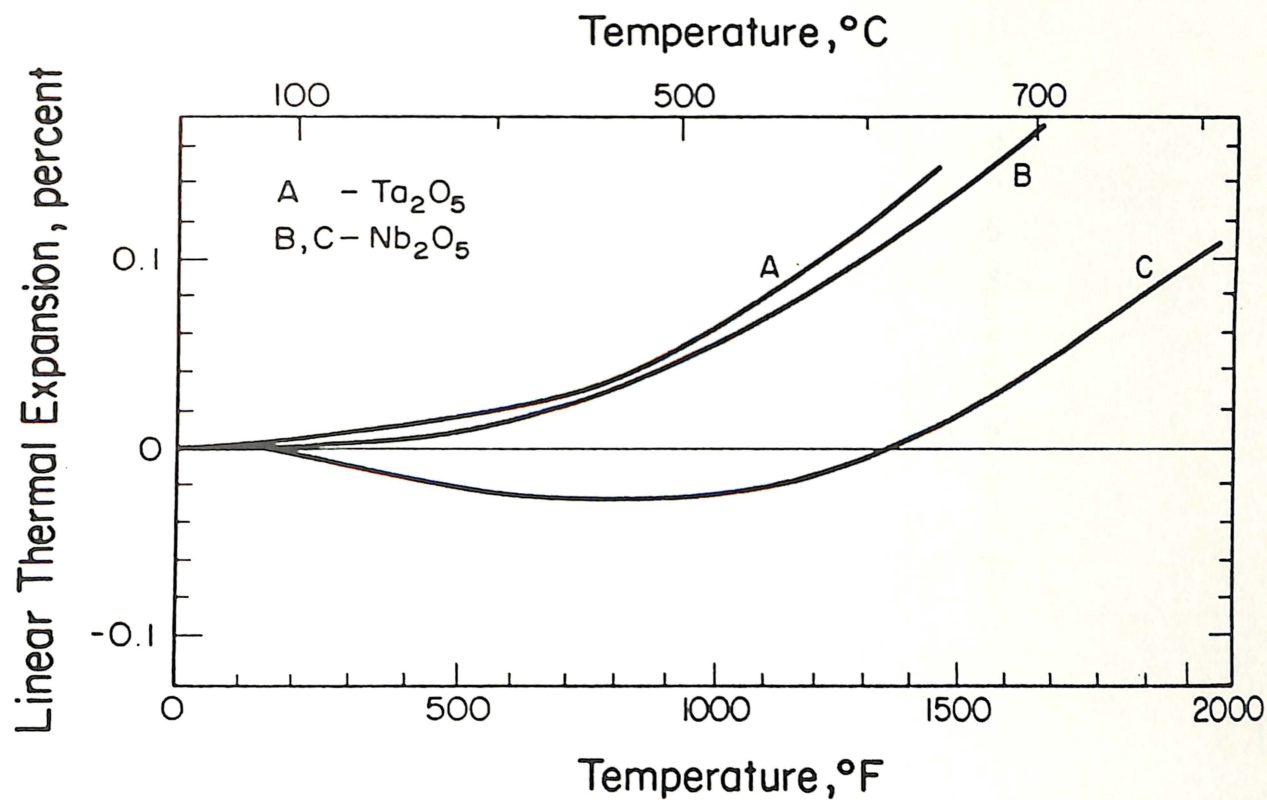


Figure 5. Thermal expansion of Nb_2O_5 (from ref. 5).

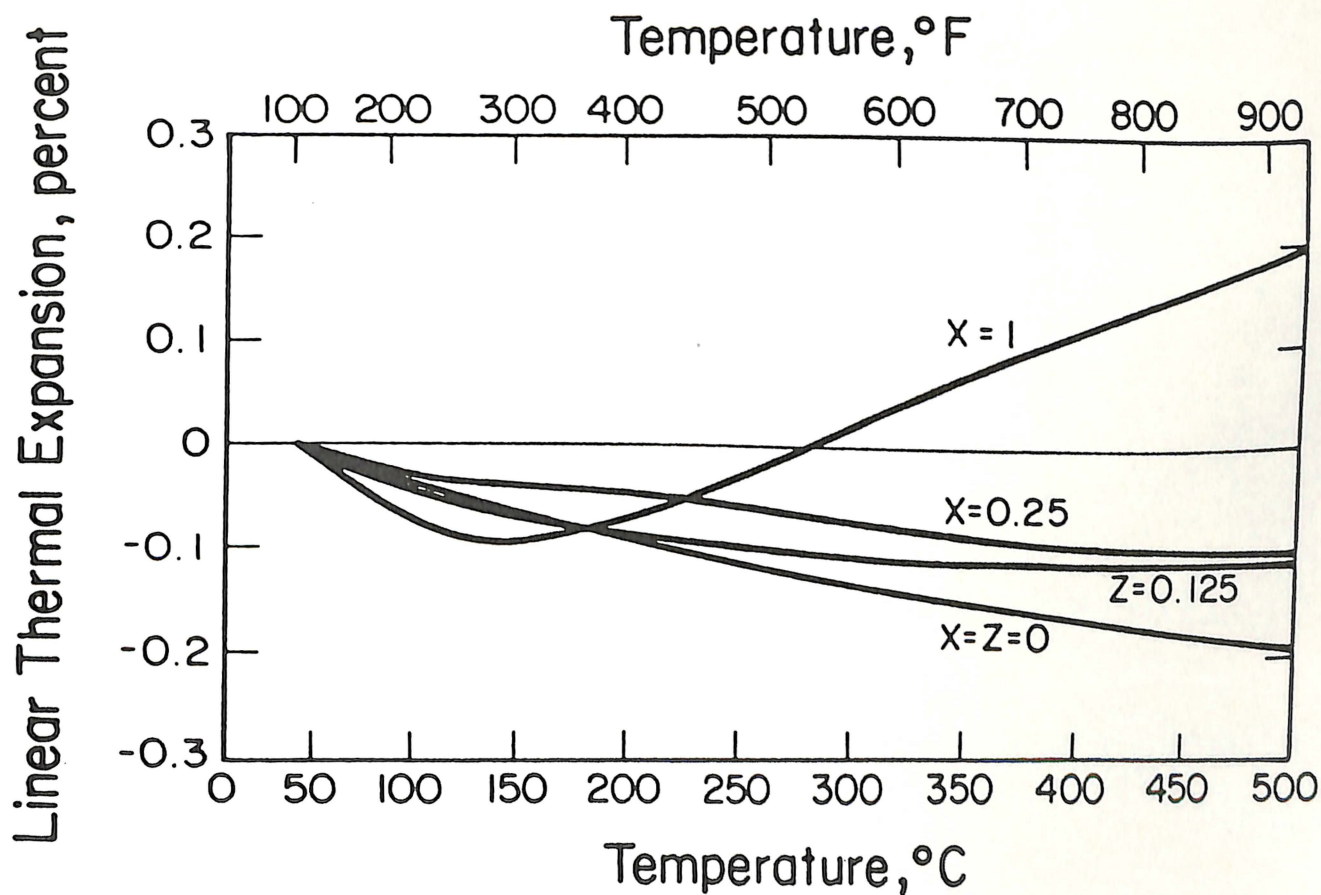
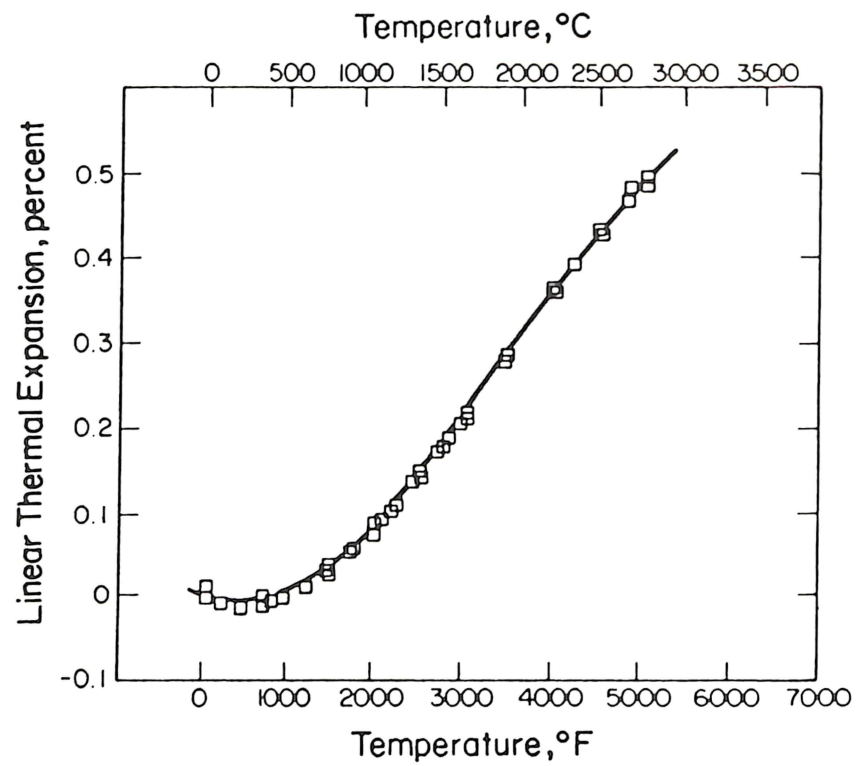


Figure 6. Thermal expansion of $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ (from ref. 15).

(a)



(b)

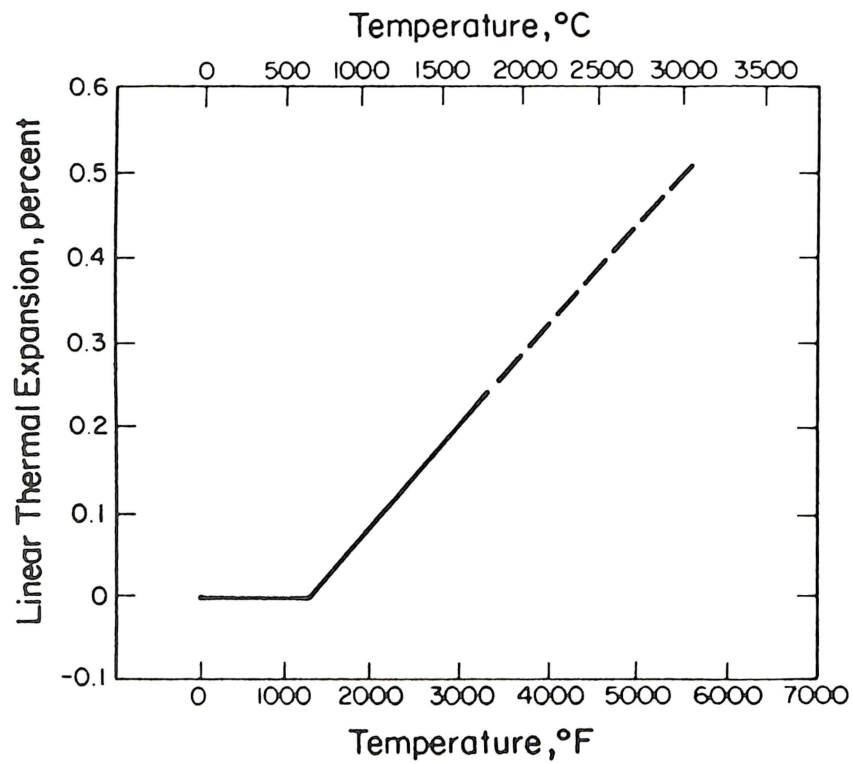


Figure 7. (a) Thermal expansion of Hitco carbon/carbon (from ref. 3);
(b) Idealized thermal expansion of carbon/carbon composite.

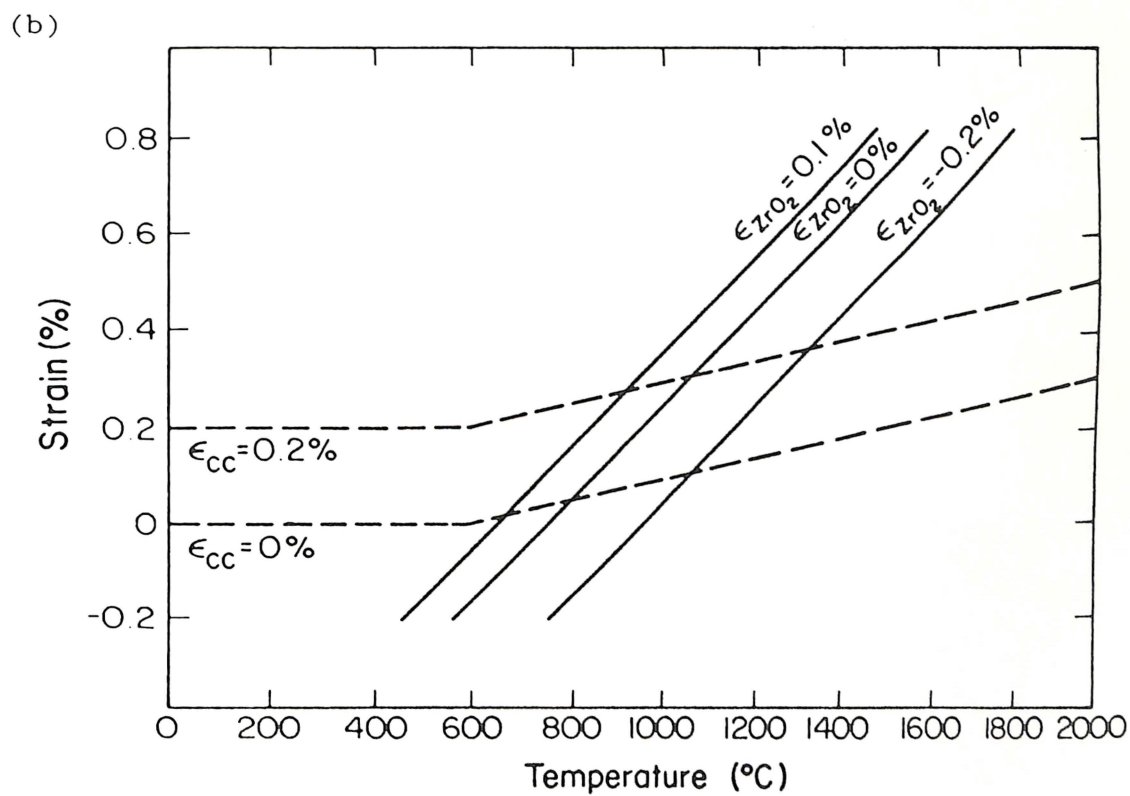
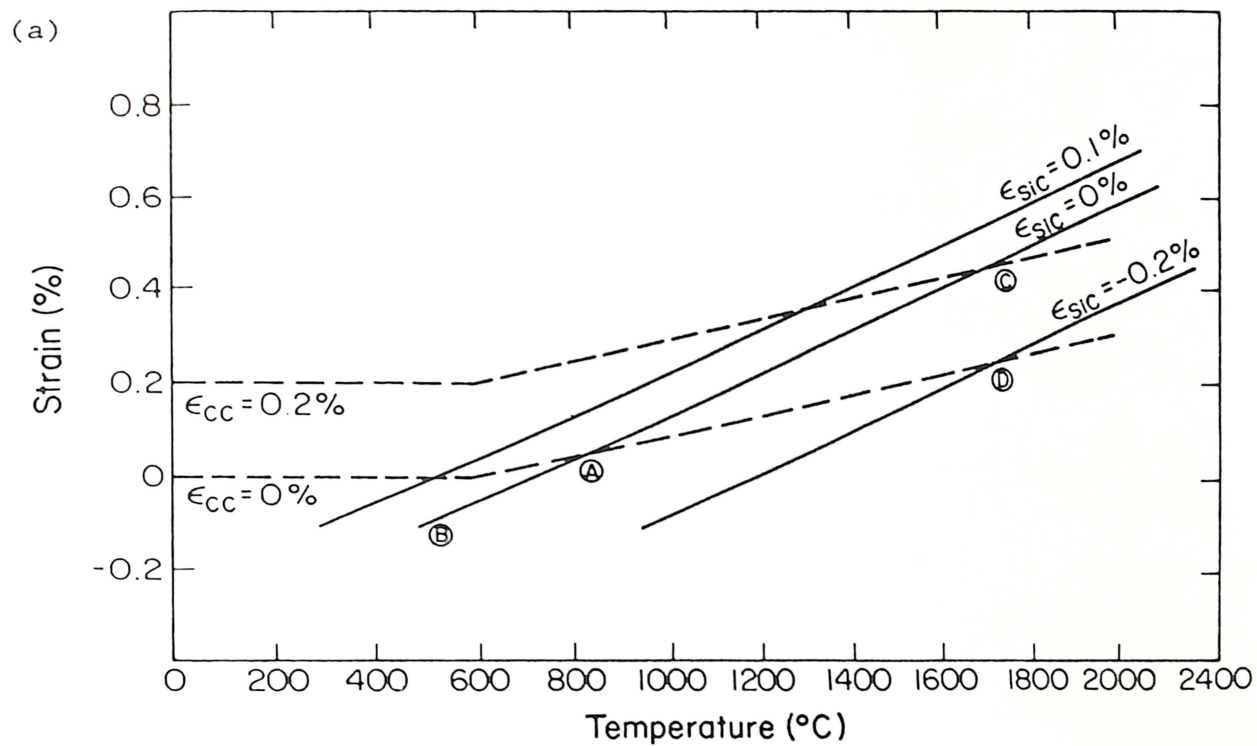


Figure 8. (a) Thermal expansion contours for SiC and carbon/carbon to determine coating strains under a variety of applied loads; (b) Thermal expansion contours for ZrO_2 and carbon/carbon to determine coating strains under a variety of applied loads.